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Potentiometric Titration of Sulfate Using A Lead-Mercury Amalgam Indicator Electrode

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POTENTIOMETRIC TITRATION OF SULFATE USING A LEAD-MERCURY AMALGAM INDICATOR ELECTRODE

by

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ABSTRACT

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by

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A lead sensitive indicator electrode was constructed with a 70 percent lead and 30 percent mercury amalgam billet. Sulfate concentrations in pure solutions, natural waters, and soil saturation extracts were determined potentiometrically using the lead-mercury amalgam indicator electrode and a standard calomel reference electrode. Sulfate concentrations over the range 0.4 to 20 milliequivalents sulfate per liter were determined with an automatic titrator and compared to a turbidimetric method for accuracy and precision. The values obtained by the two methods from twelve saturation extracts and three subsurface drainage waters were not significantly different and the potentiometric method was generally more precise. The automatic sulfate titration method has the advantages of increased sensitivity and speed.

(23 pages)

INTRODUCTION

Current analytical procedures for sulfate determination in natural waters and saturated soil extracts are either very time consuming and laborious or require specialized equipment which may not otherwise be required in a laboratory. Unless sulfate information is of particular importance it is often obtained by difference between the totals of measured anions and cations. An accurate, simple and rapid sulfate method is needed.

Recent work to speed up and simplify sulfate determinations has centered around potentiometric titrations with lead ion and measuring the increase in lead ion activity with a lead sensitive electrode as sulfate is precipitated from solution. The potential change at the lead sensitive electrode is measured using the expanded millivolt scale of a pH meter. The titration endpoint is the point of greatest voltage change with respect to titrant addition.

The objectives of the research reported herein were to construct a lead sensitive electrode and to determine its adaptability as an analytical tool to measure sulfate in natural waters and in saturated soil extracts, and to adapt the electrode for use with an automatic titrator for rapid sulfate determinations.

An electrode was constructed with a 70 percent lead and 30 percent mercury amalgam billet. The effects of carbonate, bicarbonate, chloride, nitrate, perchlorate, phosphate and silver ions, total ionic strength and pH were individually determined. Steps were taken to eliminate carbonate and bicarbonate interferences, to control pH and to

compensate for chloride effects. By being able to control or compensate for these interferences it was possible to adapt the electrode for use with an automatic titrator. This automated procedure was then compared to a turbidimetric method for accuracy and precision.

REVIEW OF LITERATURE

A variety of analytical approaches have been developed for sulfate determination. An automatic colorimetric method for measuring sulfate in water and waste discharge has been developed by Gales, Kaylor and Longbottom (1968) to be used with a Technican AutoAnalyzer. This method measures the intensity of the highly colored chloranilic acid that is released when barium chloranilate is added to a solution containing sulfate. The color intensity is proportional to sulfate present. The special manifold required for this method has a capacity of fifteen samples per hour. Sulfate or total sulfur can be determined colorimetrically by the hydrogen sulfide-methylene blue procedure of Johnson and Nishita (1952). Here the sulfate or other sulfur compounds are reduced to sulfide and determined spectrophotometrically as methylene blue. The digestion-distillation process can be completed in 2 hours. Nitrate interfers with this procedure and must be removed. Stewart and Whitfield (1965) describe a method that measures the resulting turbidity in a solution when sulfate is precipitated as barium sulfate. The turbidity is measured with a spectrophotofluorometer or a spectrophotometer. Ten to fifteen determinations can be made per hour on solutions containing as low as 1 milliequivalent (meq) sulfate per liter. Richards (1954) described a gravimetric method that requires samples containing a minimum of 5 meq sulfate per liter. This procedure requires several sample washings and is quite tedious. A more recent approach is described by Kao, Graham and Blanchar (1971). This is a radiometric procedure designed to measure barium 133 precipitated from

solution as barium sulfate. Eight sulfate determinations per hour can be made with this procedure.

In addition to the methods listed above several workers have directed their efforts toward simplifying and speeding sulfate determinations by using potentiometric titration methods. Cortellessa (1968) combusted special photographic film in small glass ampoules and titrated the resulting sulfuric acid with lead nitrate. The indicator electrode was a platinum plate and the reference electrode was a silver billet that had been immersed for 4 hours in 100 milliliters (ml) of solution containing 126 milligrams (mg) potassium hexacyanoferrate (II) and 82.2 mg of potassium hexacyanoferrate (III). Ross and Frant (1969) introduced an electrode combination with a lead sensitive indicator electrode and a double junction reference electrode which are available from Orion Research Inc.

Goertzen and Oster (1972) used the electrodes described by Ross and Frant (1969) to measure sulfate in saturated soil extracts and compared the results with those obtained by the electrical conductivity method of Lagerwerff, Akin and Moses (1965) that is designed to measure gypsum in soils. Selig (1970a) used the same electrode combination to measure sulfate oxidized from sulfur containing organic compounds.

In these potentiometric titrations the sulfate was titrated with lead ion to form lead sulfate. Lead sulfate solubility in aqueous solution is 1.4×10^{-4} molar (M) at 25 C (Weast, 1965-1966) which is too high for potentiometric titrations. Organic solvent-water mixtures suggested to lower the lead sulfate solubility include 50 percent dioxane (Ross and Frant, 1969), 60 percent dioxane (Selig, 1970a) 50 percent iso-propanol and 50 percent methanol (Cortellessa, 1968).

Goertzen and Oster (1972) found dioxane to be unsuitable because it partially decomposes into peroxide which poisons the indicator electrode. They used other solvents added to water including methanol, ethanol, n-propanol, iso-propanol, tert-butanol and acetone. Satisfactory titration curves were obtained with the first four but the largest equivalent point deflections were obtained with ethanol and methanol. A 70 percent methanol solution was used for the remainder of their work.

Interferences from chloride, nitrate, carbonate, bicarbonate, orthophosphate, cupric, mecuric and silver ions are reported by Ross and Frant (1969). They suggest that the molar ratio of chloride or nitrate to sulfate in samples should not exceed 50 to 1 and that carbonate and bicarbonate should not exceed 10 to 1 at pH 6 or 100 to 1 at pH 4. Goertzen and Oster (1972) suggest that the nitrate concentration in natural waters and saturation extracts is seldom high enough to interfere and that the high chloride effects can be compensated for by bringing the chloride-sulfate ratio in the sulfate standards into the same range as in the samples. Carbonate and bicarbonate interferences were overcome by acidification. Bradford, Bair and Hunsaker (1971) found the cupric and mecuric ion concentrations in 68 saturated soil extracts from 30 soil series to be below 0.2 and 0.011 parts per million (ppm), respectively. Goertzen and Oster (1972) indicate that 2 ppm cupric, mercuric, silver or orthophosphate-phosphorus will not interfere with the potentiometric titration and that silver and orthophosphate in soil extracts are expected to always be well below this level.

For samples containing more than 5 meq sulfate per liter the two methods compared by Goertzen and Oster (1972) agreed within 1.1 percent.

The electrical conductivity method is not expected to produce reliable results at sulfate concentrations below 5 meq/liter while the potentrometric titration should be reliable down to 0.5 meq/liter sulfate.

The individuals using the Orion electrodes all used lead perchlorate as the lead source in the titrant. Ross and Frant (1969) indicate that above 1×10^{-3}M, perchlorate is the only anion known to them that does not show at least some lead ion complexing.

Selig (1970b,1970c) has developed procedures for phosphate and oxalate determination using a lead sensitive electrode and titrating these anions with lead perchlorate.

METHODS AND PROCEDURES

A lead-mercury amalgam billet indicator electrode was constructed by adding 12 grams (g) of mercury to 28g of melted lead in a 5 ml beaker that served as a mold. A 120 x 7 millimeter (mm) pyrex glass tube with a plexiglass cap and a lead with the insulation removed from the last 30mm inserted down the center was placed half way into the molten metal (Figure 1). After the metal amalgam cooled, the glass mold was broken and removed. The billet surface was machined in a small lathe to remove surface pits caused by bubbles between the glass and the metal.

Care was taken to avoid spilling and unnecessary exposure of mercury. The lead was not heated more than necessary in order to avoid mercury distillation from the amalgam. This portion of the work was carried out in an effective fume hood. A Beckman Mercury Vapor Meter was placed in the work area to detect dangerous levels of the toxic mercury vapor. Dangerous levels were not measured.

The ionic strength, pH, and specific ion effects on the sulfate titration curves were measured by titrating sodium sulfate in solvent-water mixtures containing the factor to be studied. The titrant was made by adding lead perchlorate to the same solvent-water mixture as the samples in order to shorten mixing and reaction time. The titrant was dispensed with a 2.0 ml micrometer buret into the samples as they were mixed with a magnetic stirrer. The voltage change was measured between the indicator electrode described above and a calomel reference electrode, with the expanded millivolt (mV) scale on a pH meter.

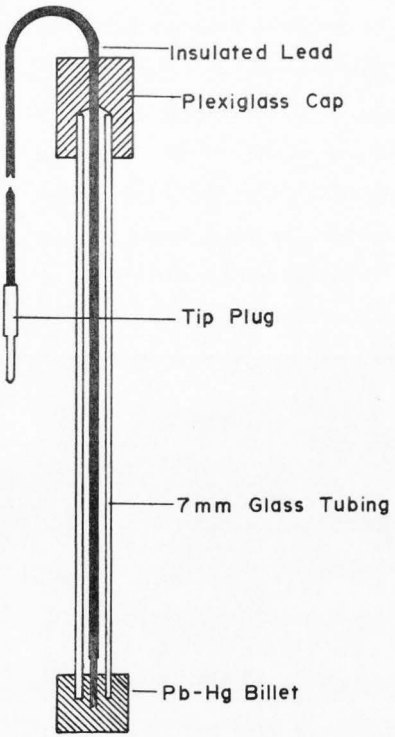

Figure I. Lead-mercury amalgam indicator electrode.

Methanol, ethanol and iso-propanol were compared as possible solvents to decrease lead sulfate solubility. Water-solvent mixtures containing 50 percent methanol or ethanol gave slightly larger equivalent point deflections than did 50 percent iso-propanol mixtures in agreement with results reported by Goertzen and Oster (1972), but the electrode response to titrant additions appeared to be more rapid in the iso-propanol-water system. For this reason a 50 percent iso-propanol-water mixture was chosen for subsequent work.

Sodium perchlorate was used to isolate the ionic strength effects of dissolved salts. Ross and Frant (1969) reported that perchlorate had no complexing effects on dissolved lead ion. Solutions containing 25 ml iso-propanol and 25 ml water that contained 0.4, 0.8, 2.0, 4.0, 8.0 or 20.0 meq sodium sulfate per liter and 0, 5 and 50 times as much sodium perchlorate as sulfate on a molar basis were prepared. These were titrated with 100 meq/liter lead perchlorate as described above.

Chloride and nitrate effects were determined in the same manner using the sodium salts and compared to perchlorate ion to distinguish between ionic strength effect and the specific ion effect.

Since carbonate and bicarbonate interferences must be removed by acidification (Goertzen and Oster, 1972 and Ross and Frant, 1969) solutions with 200 meq sodium bicarbonate and 4 meq sodium sulfate per liter were adjusted to pH 3, 3.5, 4, 4.5, 5, 5.5 and 6 to determine the pH effect on bicarbonate interference.

The equivalance point for bicarbonate determination by titration with a strong acid has a pH of 4.7. In adapting the sulfate procedure to an automatic titrator the carbonate and bicarbonate interferences were removed by titrating 40 milliliters of sample or diluted samples to

that pH on a Fisher Automatic Titralyzer with dilute perchloric acid. The sample was then brought up to 50 ml with water and 50 ml of iso-propanol was added and the solution was mixed. The samples were then titrated to -465 mV with a 50 percent iso-propanol-water mixture that contained 16 meq lead perchlorate per liter on the Fisher Automatic Titralyzer. The titrant delivery tip was placed within 1 mm of the indicator electrode billet in order for the titrator to anticipate reaching the titration end point. The titrator print delay control was set at 45 seconds because of the slower reaction time in the samples with low sulfate concentrations. The delay control is used to set the length of time delay between the last titrant addition and the titrators printing the titrant volume before proceeding to the next sample. If during this 45 seconds the voltage changes to indicate more titrant is needed then more is added and the timer resets to 45 seconds automatically.

To determine the precision of the method and to compare it with a turbidimetric method (Stewart and Whitfield, 1965), eight determinations were made on water samples from three subsurface drainage tunnels by both methods. Duplicate sulfate determinations were also made on soil saturation extracts from six horizons of an unclassified Aridisol and from the surfaces of six agricultural soils by both methods.

The double junction reference electrode suggested by Ross and Frant (1969) was compared for preformance with the calomel reference electrode used in this work.

RESULTS AND DISCUSSION

Ionic strength increases resulting from sodium perchlorate additions decreased the sharpness of the titration curves potential break. The titration of 2 meq sodium sulfate per liter in 0, 10 and 100 meq sodium perchlorate per liter is shown in Figure 2. The loss of sharpness was manifest at all solution strengths.

The lead titrant was standardized against a 2.0 meq/liter sulfate solution as shown in Figure 3. As the sulfate concentration increased a higher lead to sulfate ratio was required to reach the inflection point on the titration curve. When 0.4 meq/liter sulfate solution was titrated less titrant than expected was required to reach the inflection point and likewise more titrant than expected was required to titrate a 8.0 meq/liter sulfate solution. The inflection voltage remained the same but the titrants "effective strength" increased as more titrant was required to precipitate the sulfate in an equal volume (Figure 4). For sulfate and other nonstoichiometric titrations, Selig (1970a) suggests titrant standardization against solutions that approximate the unknowns in strength. In the work reported here standards bracketing the unknowns were used, and an "effective strength" for the titrant was determined from a curve (Figure 4) for each unknown.

Nitrate in solution at 5 times the sulfate concentration exhibited the same effect as did perchlorate at the same concentration. At 50 times the sulfate concentration, nitrate caused a greater decrease in the potential break after the inflection point was reached. As shown in Figure 5 even this effect would not be serious in the rare cases

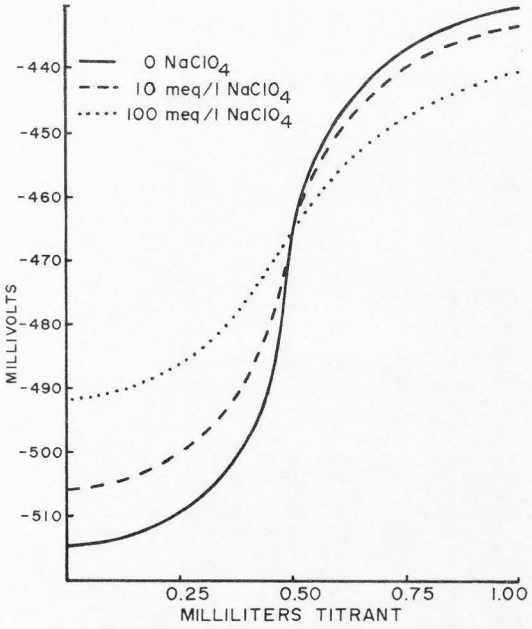

Figure 2. Titration of 0.05 meq Na_2SO_4 with 100 meq/l $Pb(ClO_4)_2$ as affected by $NaClO_4$ presence.

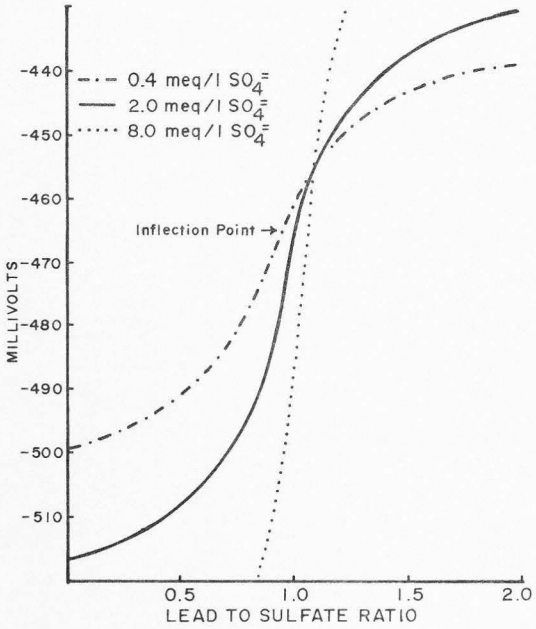

Figure 3. Ratio of lead to sulfate required to reach inflection point.

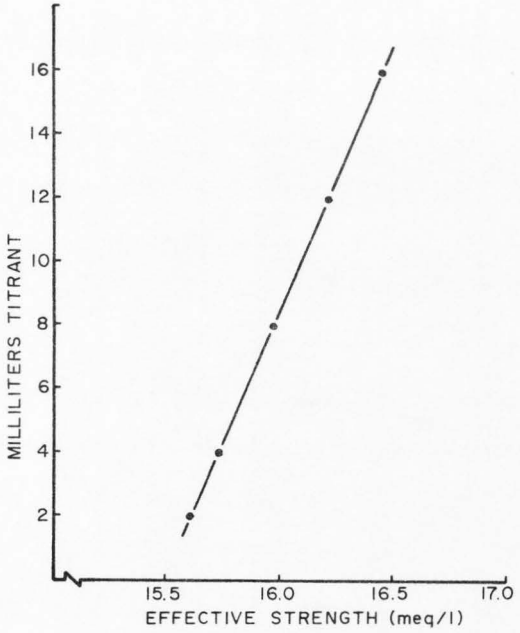

Figure 4. Increase in titrant "effective strength" with increase in titrant requirement.

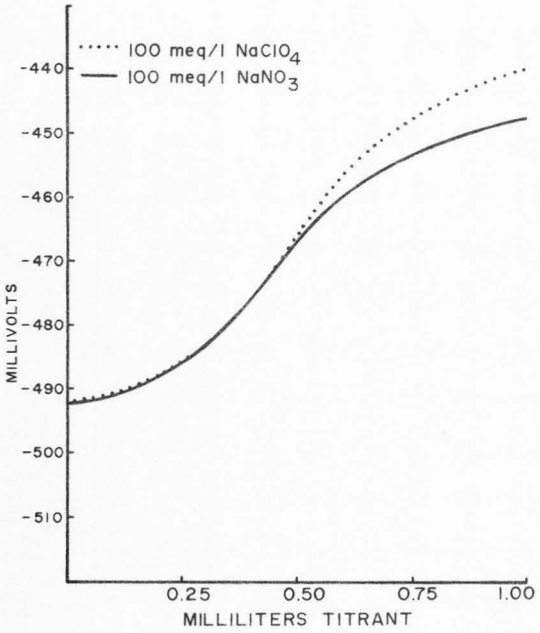

Figure 5. Titration of 0.05 meq Na_2SO_4 with 100 meq/l $Pb(ClO_4)_2$ as affected by $NaNO_3$ presence.

where nitrate was extremely high. The same pattern was observed at all sulfate concentrations tested indicating that nitrate could replace perchlorate in the titrant and in the acid for removing bicarbonate interference.

At all concentrations tested chloride interfers by shifting the titration curve to a lower voltage. Figure 6 shows this shifting when 0.05 meq of sodium sulfate is titrated in 10 and 100 meq/liter perchlorate or chloride. The shift is easily compensated for by adding chloride to the standards in approximately the same concentration as in the unknowns (Selig 1970a). Silver ion poisons the electrode and cannot be used for chloride removal.

Carbonate and bicarbonate interfere with lead titration of sulfate since lead carbonate is less soluble than lead sulfate. As the pH increases more lead carbonate forms and at pH below 3, lead acid sulfate [$Pb(HSO_4)_2$] forms (Figure 7). Since pH 4.7 is the equivalent point for bicarbonate titration with a strong acid all samples and standards were adjusted to pH 4.7 in this study.

Phosphate as indicated by Goertzen and Oster (1972) did not interfere below 0.05 meq/liter but 4 meq/liter in 4 meq/liter sulfate interfered by forming insoluble lead phosphate. Phosphate in natural waters and soil extracts is rarely over 0.05 meq/liter and would not be expected to interfere.

Silver ion below 0.01 meq/liter did not interfere with the sulfate titration but 4 meq/liter poisoned the electrode and it was necessary to remove a very thin metal layer from the electrode surface before it would respond again. Silver in soil saturation extracts and natural waters will seldom exceed 0.01 meq/liter (Goertzen and Oster 1972).

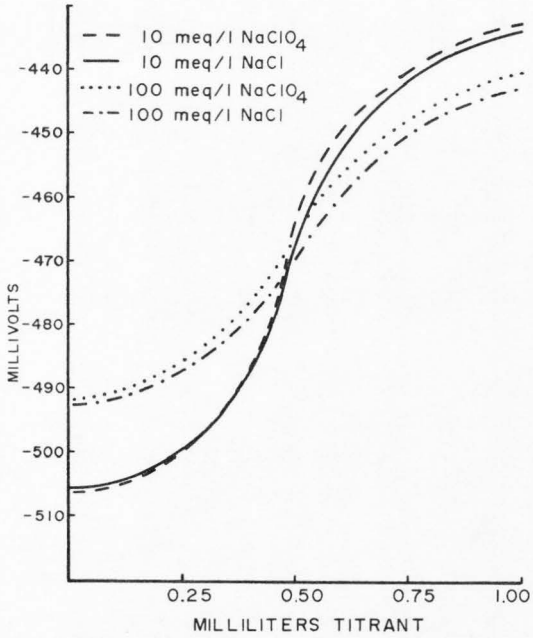

Figure 6. Titration of 0.05 meq Na_2SO_4 with 100 meq/l $Pb(ClO_4)_2$ as affected by NaCl presence.

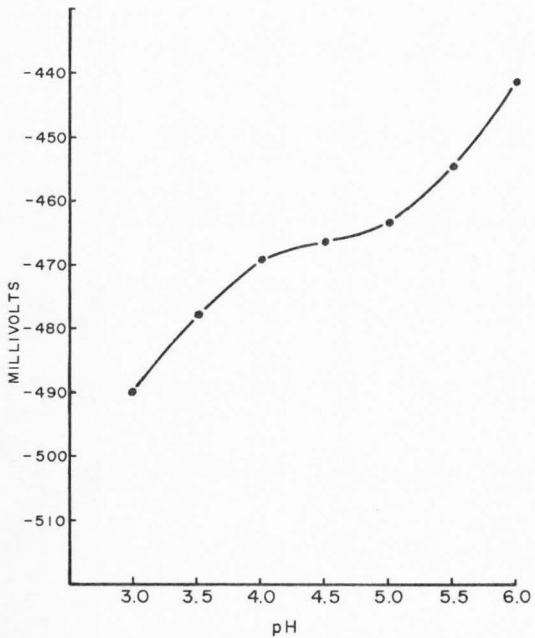

Figure 7. Inflection point voltage as affected by pH adjustment of sample containing 200 meq/l $NaHCO_3$ and 2 meq/l Na_2SO_4.

Figure 8 shows the titration curve for a subsurface drainage water and Figure 9 is the curve for a saturated soil extract. The samples were adjusted to pH 4.7 with perchloric acid and titrated manually.

Eight sulfate determinations were made turbidimetrically and compared to eight potentiometric determinations made using a Fisher Automatic Titralyzer on samples from three subsurface drainage sites. The mean, standard deviation and coefficient of variation are shown for each site and method in Table 1. The potentiometric method is more precise than the turbidimetric method. Carbonate and bicarbonate determinations were made at a rate of 30 to 50 per hour and 25 to 30 sulfate determinations were made per hour using the automatic titration procedure.

Table 1. Results from eight sulfate determinations by two methods on three subsurface drainage waters.

	Sulfate	Standard Deviation	Coefficient of Variation
	meq/l		Percent
Sample Site			
Method			
Fish Hatchery			
Turbidimetric	2.08	0.11	5.47
Potentiometric	2.01	0.02	1.15
Hankins			
Turbidimetric	3.29	0.27	8.21
Potentiometric	3.38	0.05	1.55
Tolbert			
Turbidimetric	4.50	0.15	3.42
Potentiometric	4.20	0.17	4.06

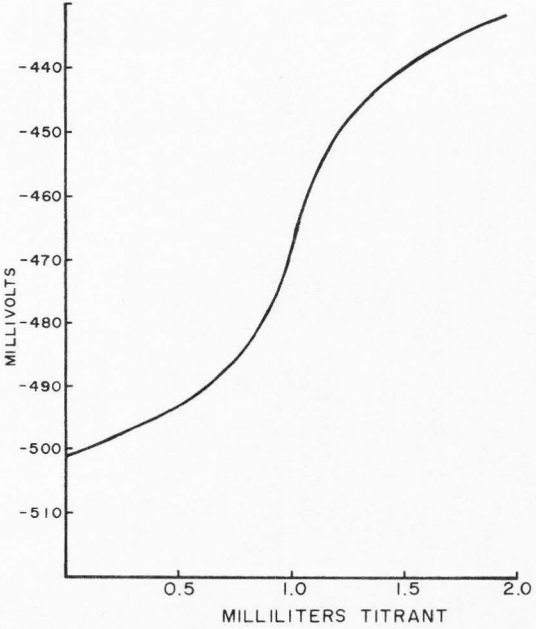

Figure 8. Twenty-five ml sample from Tolbert drainage tunnel titrated with 100 meq/l $Pb(ClO_4)_2$.

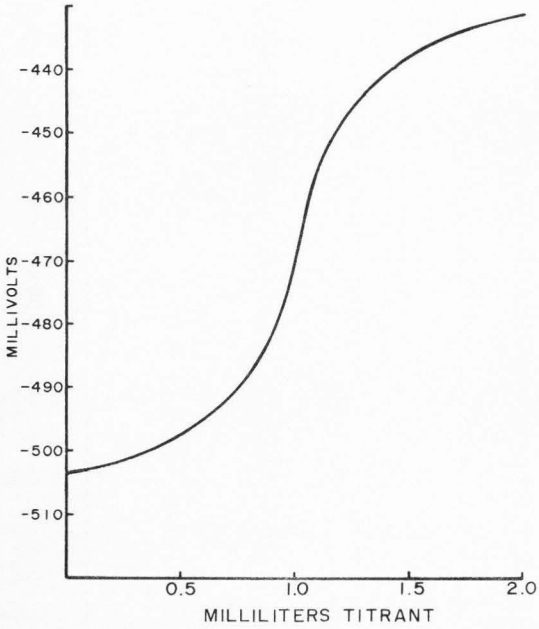

Figure 9. Ten ml sample Minidoka silt loam saturated soil extract diluted to 25 ml and titrated with 100 meq/l $Pb(ClO_4)_2$.

Duplicate sulfate determinations on saturated soil extracts from six horizons of a noncultivated Aridisol (Natragid) and six cultivated soil samples are shown in Table 2. Results from the two procedures did not differ significantly.

The double junction reference electrode suggested by Ross and Frant (1969) was compared with the calomel reference electrode used for performance and reference voltage. No difference was found and the result indicates either reference electrode can be used effectively.

The lead-mercury amalgam indicator electrode used in this work had a lower voltage over the entire curve than the commercially available

Table 2. Sulfate analysis by potentiometric titration and turbidimetric methods on saturated extracts from six horizons of a non-cultivated Aridisol (Natragid) and six cultivated soils.

Description		EC x 10^{-3}	Sulfate potent.	Sulfate turbid.
		mmohs/cm	meq/liter	
Non-cultivated Aridisol				
Depth, cm	Horizon			
0 - 1	A-2	1.6	1.77	1.50
1 - 13	B-21	7.7	23.10	21.50
13 - 35	$B\text{-}22_{sa}$	16.5	90.91	89.13
35 - 45	$C\text{-}1_{casa}$	15.8	77.99	79.75
45 - 50	$C\text{-}2_{casa}$	13.3	76.46	74.75
50 - 60	C_{cam}	6.2	64.50	64.25
Cultivated Soils (Surface 10 cm)				
Portneuf		1.1	3.25	2.85
Minidoka		3.3	10.89	11.60
Purdam		5.0	0.51	0.37
Scism		2.8	7.17	7.45
Greenleaf		1.4	2.33	2.00
Nyssaton		1.2	3.89	3.83

lead sensitive electrode. The inflection point voltage for the lead-mercury amalgam electrode was -467 mV while the endpoint shown by Ross and Frant (1969) was about -125 mV and that shown by Goertzen and Oster (1972) was about -195 mV.

The lead-mercury amalgam electrode response to lead ion additions into a sulfate-containing solution is not instantaneous but is sufficiently rapid to be used with an automatic titrator.

The electrode is easily cared for. Precipitate removal from the billet with a paper towel after each days use was the only maintainance required.

SUMMARY

The objectives of this study were to construct a lead sensitive electrode and to determine its adaptability as an analytical tool for measuring sulfate in natural waters and in saturated soil extracts.

An electrode with a 70 percent lead and a 30 percent mercury amalgam billet was constructed. Sulfate determination interferences commonly found in water samples and soil extracts were determined and steps were taken to remove or compensate for the interferences. The potentiometric sulfate titrations with lead perchlorate were carried out in 50 percent iso-propanol solutions. Procedures were developed to adapt the potentiometric titration method to sulfate analysis with an automatic titrator.

The automatic titration method was generally more precise than the turbidimetric method to which it was compared. Carbonate and bicarbonate determinations were made at a rate of 30 to 50 per hour and 25 to 30 sulfate determinations were made per hour using the automatic titration procedure. The results obtained by the two methods were not significantly different when sulfate was measured in three water samples and twelve saturated soil extracts.

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